Electrochemical hydrogenation after mechanical activated near equiatomic Ti-Ni powder

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Abstract. It has been studied an effect of mechanical activation in a planetary ball milling on the electrochemical hydrogenation of Ti-Ni powder near equiatomic content. It has been shown that average particle sizes measured by scanning electron microscope decreased from 11.1 to 7.8 μm up to 30 s mechanical activation, then increased to 33.2 μm for 300 s activation. Beside, with an increase in the time of mechanical activation was formed state with small the coherently diffracting domain which correspond to quasi-amorphous state of material. It has been shown that after hydrogenation, the particle size distribution did not change. There is an incubation time hydrogenation for mechanical activation, when hydrogenation is not occurring. Mechanical activation for more than 30 s leads to the formation of the Ti_2NiH_x phase based on the Ti_2Ni and 50 s activation is sufficient to form the $Ti_2NiH_{0.5}$ stoichiometry. For a longer mechanical activation a phase with the stoichiometry $Ti_2NiH_{0.85}$ was formed and to obtain the Ti_2NiH stoichiometry it is necessary to carry out activation for 4.5 hours.

1. Introduction

Titanium – nickel alloys are perspective materials for applications in rechargeable nickel-metal hydride batteries due to their high volume density of hydrogen, small density, high electrochemical activity and corrosion resistance.

The system Ti-Ni near equiatomic composition as a rule has a complex phase content consisting with TiNi with BCC (B2), Ti_2Ni with FCC ($E9_3$) and $TiNi_3$ with HCP ($D0_{24}$). The intermetallic compound of Ni_3Ti is not capable for hydrogen storage [1-3], while the intermetallic compounds of TiNi [4] and Ti_2Ni [5] can absorb a great amounts of hydrogen. Ti_2Ni and TiNi absorbs a large amount of hydrogen by gas-solid reaction [6-8]. Besides this Ti_2Ni has four hydride phases ($Ti_2NiH_{2.5}$, Ti_2NiH_2, Ti_2NiH and $Ti_2NiH_{0.5}$), whilst TiNi has only one hydride phase, TiNiH [5].

According to the literature, the interaction of hydrogen with a metal may be accompanied by a change in the lattice parameter [9], e.g. Pelton, *et. al,* [10] showed that the presence of hydrogen increases the lattice parameter of the B2 phase from 0.3025 nm to 0.3047 nm (2.2 % volume increase). Buchner, et al. [5] have detected that the lattice parameter of the B2 structure increased from 0.301 nm to 0.310 nm, which corresponds to a volume increase of nearly 10 %, the lattice parameter increases due to the occupation of hydrogen an interstitial lattice site.

As it well known increasing of density of defects in materials ensured by the penetration of hydrogen via lattice defects [11]. A high-energy mechanical activation (MA) is used to increase a density of defects [12-14] and similar treatment is a very effective for powders. There are several

methods of hydrogenation, for powders a simplest technique is electrochemical hydrogenation, when hydrogen is generated via electrochemical reaction in special solutions [15, 16].

The aim of this paper is to study the effect of mechanical activation on electrochemical hydrogen saturation of near equiatomic Ti-Ni powder.

2. Material and methods

The tests were performed using near equiatomic $Ti_{0,45}Ni_{0,55}$ powder, produced by the «Polema» plant. The mean size of particles 22 μm (standard deviation, sd=10 μm). Mechanical activation was carried out using a planetary ball mill «AGO-2», an acceleration during treatments was 60 g and the milling time was 5 – 300 second.

For the electrochemical hydrogenation of powders a special cell, figure 1, has been constructed. A 20 % aqueous solution of NaCl with the addition of 1.5 g/l of dextrin as surfactant served as electrolyte. The cathode current density during the experiment was 40 - 70 mA/cm^2. The temperature of the electrolyte was constant, approximately 20 °C. The absorption of hydrogen by metal occurs slowly in the first minutes (up to 30 minutes) of hydrogenation. This effect is associated with an oxide layer on the metal surface. An increase in time of 0.5 to 10 hours leads to a sharp increase in the rate of hydrogen absorption. In particular, the hydrogen content does not change significantly from 90 minutes to 10 hours with maximum absorption of hydrogen [17]. Thus, the hydrogenation time was 90 minutes.

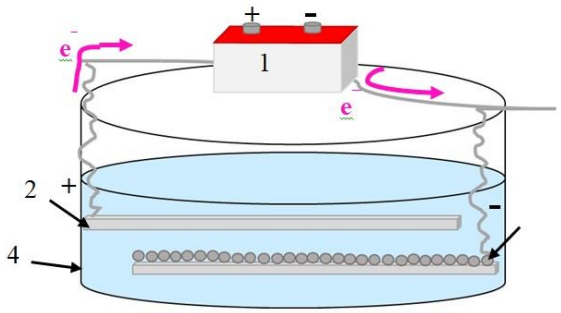


Figure 1. Basic outline of electrochemical hydrogenation : 1 – current source ; 2 – anode (graphite plate); 3 – cathode (TiNi powder immersed in a stainless steel cup); 4 – working vessel

Investigations of particle morphology and its size distribution were performed by scanning electron microscopy (SEM) TESCAN VEGA 3SBH and laser diffraction (LD) methods using a SALD-7101 nanoparticle diffraction analyzer by Shimadzu (Japan). The dispersion liquid was 0.2 wt. % aqueous solution of sodium citrate $Na_3C_6H_5O_7$.

Analysis of the phase composition and the parameters of the crystal structure of the powder were carried out by X-ray diffraction (XRD) on diffractometer with Cu-Kα filtered radiation with statistics accuracy better than 0.5 %.

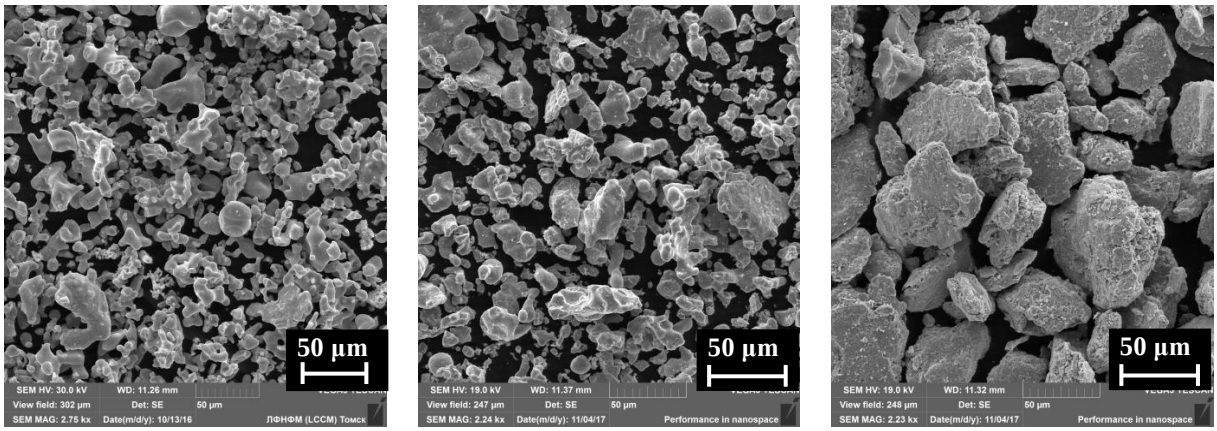
The specific surface area (SS) of the powder was measured by the BET [18] method by Sorbi series instrument. From the obtained values of the specific surface it has been calculated the average particle size assuming their spheroids shapes.

3. Results

3.1. Morphology and particle size

The SEM pictures of powders are shown in figure 2. The particles mean size and size of the coherently diffracting domain (CDD) are shown in Table 1. As one can see, there are two stages during treatment: on the first step up to 30 s the fracture process of particles which changes agglomeration stage after this. The SEM and SS dat have shown that internal structure became more dispersive.

It was remarkable, that morphology and particle size distribution of powders do not change after hydrogenation.



(a) (b) (c)

Figure 2. SEM micrographs of the powder in the initial state (a) and after mechanical activation of 30 s (b) and 300 s (c)

Table 1. The particles mean size and size of the coherently diffracting domain (CDD)

Mechanical activation time, s	$<d_{SEM}>$ (μm), St.dev. (μm)	$<d_{LD}>$ (μm), St.dev. (μm)	SS ($m^2 \cdot g^{-1}$), Error ($m^2 \cdot g^{1}$) / $<d_{BET}>$ (μm), St.dev. (μm)	CDD (nm)
0	11.1±7.5	7.9±0.2	0.24±0.02 / 3.9±0.43	43
10	11.0±7.6	7,6±0.3	0.28±0.02 / 3.3±0.20	21
30	7.8±6.6	6.1±0.2	0.37±0.01 / 2.5±0.01	17
60	13.8±9.8	6.0±0.2	0.49±0.04 / 1.9±0.04	8
300	33.2±25.7	0.5±0.2	0.54±0.02 / 1.7±0.09	5

3.2. X-ray analysis

In figure 3a are shown X-ray patterns of powders in initial state and after mechanical activation. As one can see after mechanical activation, powder consist of TiNi (B2) and $NiTi_2$ ($E9_3$); TiNi (B19`) and Ni_3Ti ($D0_{24}$). In the process of mechanical activation, width of the peaks increase and after 200 s X-ray patterns looks like belongs to quasi-amorphous state of material, Figure 3a, and separate lattice parameter of phases could not be determined.

The phase content of the powder did not change after hydrogenation, figure 3b. After hydrogenation lattice parameters of all phases except of Ti_2Ni did not change, but for Ti_2Ni there is significant changing of lattice parameter, figure 4. From this figure one can see increasing this value from 1.132 nm to 1.163 nm, i.e. increasing by a factor of 3.1 %.From this plot one can conclude that after mechanical activation the lattice parameter does not changes and correspond to the table value, dashed black line [pdf2 №72-0442]. After hydrogenation parameter increase for samples activated more when 30 s reached $Ti_2NiH_{0.5}$ stoichiometry (blue dashed line) [pdf2 №27-0346] and more up to $Ti_2NiH_{0.85}$. Approximation of dependence of the lattice parameter of the $NiTi_2$ phase on the time of mechanical activation allowed us to obtain the equation $y = 0.1194\tau^{0.0052}$, which can be used to determine the hydrogen content achieved in the process of hydrogenation, figure 4b. Extrapolation of this dependence had shown that in order to obtain the Ti_2NiH_1 stoichiometry with the lattice parameter [19], it is necessary to carry out a mechanical activation for 4.5 hours. Unfortunately, this time is too long for such treatment. From figure 4 one can see that lattice parameter of Ti_2Ni after hydrogenation did not change (until 10 s mechanical activation). Accordingly the penetration of hydrogen via lattice defects does not observe. So, there is some «incubation period», for these experiments the value was a 10 s of mechanical activation.

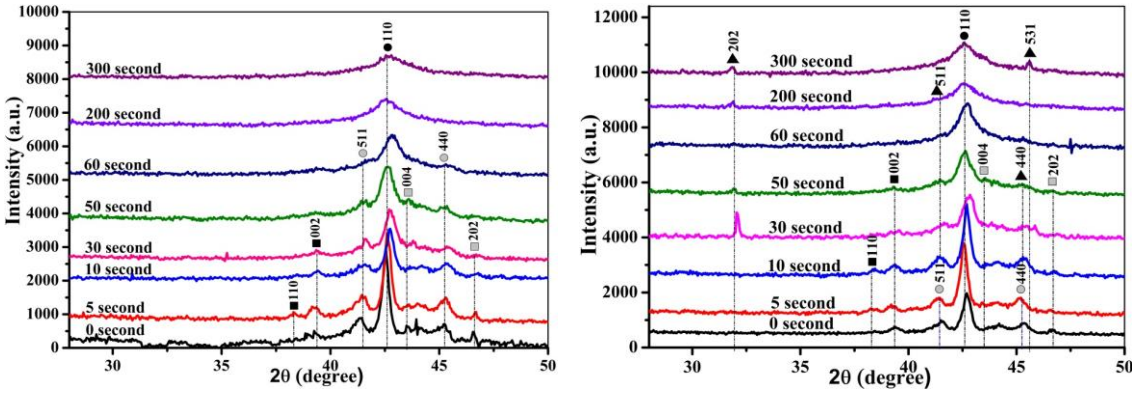


Figure 3. XRD patterns of TiNi powders before (a) and after (b) hydrogenation with different mechanical activation time.
● – TiNi (B2); ■ – TiNi (B19`); ● – Ti_2Ni ($E9_3$); ■ – Ni_3Ti ($D0_{24}$); ▲ – Ti_2NiH_x ($E9_3$)

Probably it's connected to destruction of thin oxygen layers on the particles surfaces which removed during hydrogenation. So increasing of time hydrogenation (more 90 min) will allows reduce or remove “incubation period” of hydrogenation. But more likely hydrogen absorption are connected with defects accumulation during activation and such “incubation period” will not observe in all experiments, since, the hydrogen atoms may additionally be trapped via defects [20-23], which can provide access for the rapid diffusion of H-atoms [14], but it should be investigated in the following studies.

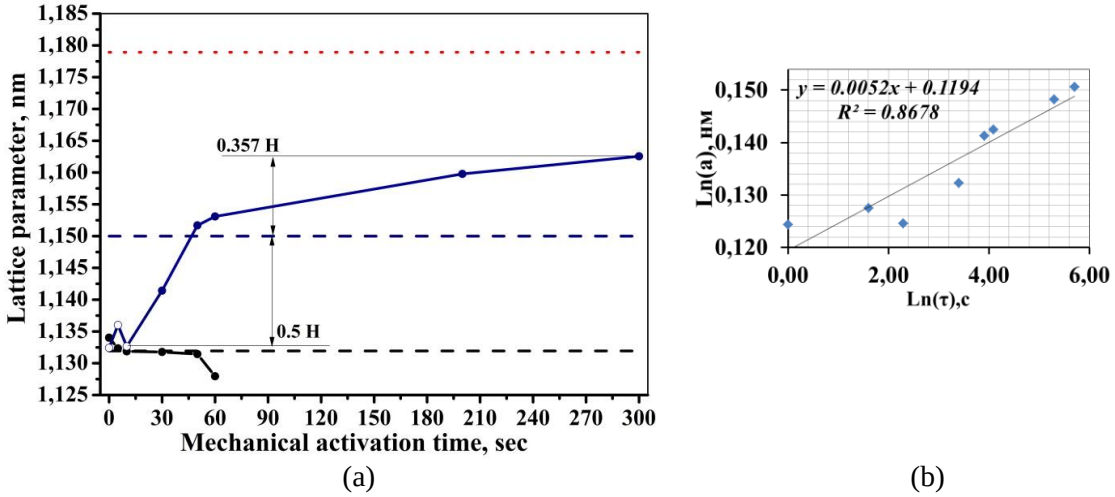


Figure 4. Dependence of the lattice parameter of the $NiTi_2$ phase on the time of mechanical activation before and after hydrogenation (a); approximation of the dependence of the lattice parameter of the $NiTi_2$ phase on the time of mechanical activation of the powder after hydrogen absorption (b).
▬ ▬ - $NiTi_2$ pdf2 №72-0442; ▬ ▬ - $Ti_2NiH_{0.5}$pdf2 №27-0346; ---- - Ti_2NiH_1 ASTM [8]; ▬●▬ - Ti_2Ni before hydrogenation; ▬○▬ - Ti_2Ni after hydrogenation; ▬●▬ -Ti_2NiH_x after hydrogenation

Based on these results, one can assume that mechanical activation will allow obtaining a large capacity of hydrogen in this multiphase system.

4. Conclusion

With an increase in the time of mechanical activation, a state with a very small CDD is formed, which may correspond to quasi-amorphous state of material. CDD size is significantly less than <d> (LD and BET), that is, the powder particles consist of several crystallites, the number of which increases on average from 5×10^4 to 13×10^6 with increasing time of mechanical activation. There is an incubation time of hydrogenation when hydrogenation is not occurring. Mechanical activation for more than 30 s leads to the formation of the Ti_2NiH_x phase based on the Ti_2Ni and time 50 s is sufficient to form the $Ti_2NiH_{0.5}$ stoichiometry. Longer mechanical activation allows forming a phase with the stoichiometry $Ti_2NiH_{0.85}$.

Acknowledgement

This work was carried out according to the Program III.23 of Fundamental Scientific Research of the State Russian Academy of Sciences for 2013-2020. Authors are grateful for Leonov A. for his help in analyzing the particle size distribution in TPU Nano-Center.

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